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Gas Evolution and Self-Discharge in Li/MnO$_2$ Primary Batteries

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ARL-TR-1805   December 1998

Army Research Laboratory

Adelphi, MD 20783-1197

Gas Evolution and Self-Discharge in Li/MnO$_2$ Primary Batteries

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Abstract

A survey is presented of the available literature on the problem of gas evolution in the Li/MnO_2 primary battery system during storage. This gassing is due to the breakdown of the solvents, primarily propylene carbonate (PC) and dimethoxyethane (DME). Of these, the major contributor to gassing during storage is PC, which undergoes a hydrolysis reaction to form CO_2. This reaction is a function of the amount of absorbed and structural water. Techniques to help eliminate gassing during storage include predischarging and the use of water scavengers, cathode additives, reactive dehydration, properly heat-treated MnO_2, weak oxidizing salts, and oxidation-resistant solvents.

Although not a major factor in gas evolution in stored batteries, DME has been observed to form methane (CH_4) during discharging, probably via an oxidation reaction that is ultimately a function of the absorbed water content.

The report also briefly reviews the self-discharge characteristics of Li/MnO_2. Three factors determine the self-discharge of Li/MnO_2:

- The oxidation state of the manganese ion. For the types of MnO_2 used, it is expected that the self-discharge rate would be low.

- The nature of the electrolyte salt and amount of absorbed water. Self-discharge is higher for $LiClO_4$ and $LiCF_3SO_3$ electrolytes than for fluorinated salt electrolytes.

- The nature of the solvent. Self-discharge is higher for ethers (e.g., DME) than for carbonates (e.g., PC).

Contents

Table

1. Introduction

Manganese dioxide (MnO_2) is one of the most important cathode materials used in both aqueous and nonaqueous batteries [1–12]. Nonaqueous primary batteries with lithium anodes and manganese dioxide cathodes have been widely used in commercial applications since the early 1980s, because of their high energy density, good rate capability, low-temperature performance, long shelf life, and competitive cost [2,4].

Generally, Li/MnO_2 primary batteries are housed within a metal container. However, the U.S. Army has recently become interested in the concept of a pouch cell for Li/MnO_2 primary batteries. The pouch cell consists of the internal components sealed within a multilaminate of polyester, polyethylene, aluminum, and surlyn [13,14]. Compared to metal containers, pouch cells reportedly [13] offer the advantages of (i) weight savings and (ii) improved safety. The pouch cell poses several problems that were insignificant or did not occur for Li/MnO_2 batteries housed in metal containers. One of these is the swelling of the pouch cell as a result of gassing during storage before use [14].

This report presents a summary of the available literature to assist in the identification of potential reasons for the swelling (gassing) of the Li/MnO_2 pouch cells during storage. We also present a brief review of the self-discharge characteristics of Li/MnO_2.

2. MnO_2 Background

The electrochemical properties of the Li/MnO_2 system are a strong function of the structure and physiochemical properties of the MnO_2 cathode [1–9]. Hence, swelling and self-discharge problems may also be a function of these same properties. Here we briefly review the structural, physiochemical, and electrochemical properties of MnO_2.

2.1 Structure

At present, the three most important MnO_2 polymorphs for Li primary batteries are β-MnO_2 (pyrolusite), ramsdellite, and γ-MnO_2 [2,4,5,15–19]. These different polymorphs can be described in terms of octahedra composed of oxygen atoms with manganese atoms in the center. The different structural forms are built up by the octahedra linked together in various ways:

- The β-MnO_2 polymorph, whose structure is a tetragonal lattice, consists of single chains connected by corner sharing to other single chains. The [1×1] channels in the hexagonal oxygen matrix can be observed.

- Ramsdellite, whose structure is an orthorhombic lattice, consists of double chains of octahedra connected to other double chains by corner sharing. The ramsdellite structure contains [1×2] channels.

- Finally γ-MnO_2 is the best-known polymorph used in Li primary batteries. The γ-MnO_2 polymorph does not represent a specific crystal structure of MnO_2 [5]; instead, it consists of a random intergrowth of pyrolusite and ramsdellite, with ramsdellite being the majority phase [7,9].

2.2 Preparation

The γ-MnO_2 polymorph that is used for lithium primary batteries is synthesized either by electrolytic or chemical methods. Electrolytic methods are usually preferred because the resulting material has greater surface area and higher purity [4,17,19]. However, the results of Amlie and Tvarusko [20] revealed that chemical γ-MnO_2 (CMD) exhibited a larger surface area than electrolytic γ-MnO_2 (EMD). EMD is produced by anodic oxidation of an Mn^{+2} salt (e.g., $MnSO_4$) in an acidic medium. CMD, in contrast, can be obtained by many different synthesis routes [11], including (i) thermal decomposition of manganous nitrates, (ii) oxidation of manganous hydroxide, (iii) oxidation of manganous carbonate, (iv) oxidation of manganous salts by oxidizing agents such as ammonium chlorate, and (v) reduction of permanganates in a boiling solution of manganous sulfate. Of the chemical methods, the one most preferred for battery cathodes is the oxidation of manganous carbonate [11].

A third method of obtaining γ-MnO_2 is by acid digestion of $LiMn_2O_4$ [17]. This method also has advantages (see sect. 2.4).

2.3 H_2O Content

One of the most important variables determining electrochemical behavior that is related to the swelling (gassing) problem is the water content of the MnO_2. When we specify water content, we must first define the type of water and its behavior under heat treatment.

In MnO_2 there are two types of water: absorbed and structural [2,4,5,10,20–24]. Physically absorbed or surface water is associated with neutral water molecules that are hydrogen bonded to underlying OH^- groups [10,22]. Physically absorbed water can be removed by the MnO_2 being heated in air at 110 °C. On the other hand, the structural or chemically combined water is present in the lattice and requires heating to several hundred degrees Celsius to be completely eliminated.

Structural water is present in the MnO_2 lattice as OH^-, since the water molecule is much larger than the [1×1] channels in pyrolusite and the [1×2] channels in ramsdellite [25,26]. Charge neutrality requires that if an OH^- substitutes for O^{-2} in the lattice it must be compensated by either an

Mn^{+4} vacancy or an Mn^{+3} ion [26]. In either case, the presence of structural water as OH^- reduces the number of Mn^{+4} ions. As the concentration of Mn^{+4} ions in MnO_2 decreases, the capacity decreases (see sect. 2.5). Reutschi [25] has suggested that for charge compensation by Mn^{+4} vacancies ([Mn^{+3}] = 0), 4 wt.% structural water will reduce the capacity of MnO_2 by 10 percent, whereas 8 wt.% structural water will reduce the capacity by 20 percent (of the theoretical value for MnO_2 containing no structural water).

The total water content (absorbed + structural) for both EMD and CMD is typically between 4 and 8 wt.% [4,21,24]. The amount of physically absorbed water is slightly lower for EMD than for CMD. For structural water, there are contradictory reports as to whether CMD [4,24,25] or EMD [21] has lower content. For both CMD and EMD, the amount of water (structural) remaining after the 110 °C heat treatment is about 70 to 80 percent (2 to 6 wt.% water) out of the total water content [4,21]. Ikeda et al [2,4] revealed that both CMD and EMD must be heated to 750 °C for all the structural water to be removed. This temperature is above that at which the phase transformation of MnO_2 to Mn_2O_3 occurs ($\approx$550 °C [10]). Therefore, heat treatment alone is not an acceptable method for obtaining water-free MnO_2.

2.4   Heat Treatment

Before being used as cathodes in Li primary batteries, both EMD and CMD are typically heat-treated in the range from 300 to 430 °C, typically between 350 and 400 °C [1–9]. Heating above 400 °C results in a loss of capacity due to a loss of oxygen from MnO_2 [2,4,5]. Heat treatment in the range from 350 to 400 °C removes all the absorbed water and most of the structural water (70 to 80 percent [4]), resulting in a modification of the structure for both EMD and CMD. However, the core structure of EMD and CMD does not change on heating [7,9]. As the temperature is increased, only the relative amounts of pyrolusite and ramsdellite change. With increasing temperature, the relative amount of pyrolusite increases. In the temperature range between 350 and 400 °C, it has been reported that MnO_2 consists of (i) only β or (ii) "γ/β" (a mixture of ramsdellite and pyrolusite, with pyrolusite the majority component [1–9]). The heat-treated MnO_2 is usually mixed with a conductive agent and binder, and this mixture is then heated in the temperature range from 200 to 350 °C (so that water is eliminated from the surfaces of the binder/conductive agents and reabsorbed water from the MnO_2 surface) before insertion in the cell as a cathode [2,4].

In addition, after the high-temperature heat treatment, the surface area is reduced. Ikeda [4] observed that after the 400 °C heat treatment, the surface area of EMD decreased by about 47 percent and that of CMD by 33 percent.

The γ-MnO_2 that is formed by acid digestion of $LiMn_2O_4$ is typically heated in the range from 300 to 350 °C and transforms to β-MnO_2. The total water content of this material after heat treatment is much less (0.1 wt.%) than for EMD and CMD (1 wt.%) after similar heat treatment [17].

It is important to note that β-MnO_2 synthesized directly by chemical methods (e.g., thermal decomposition of manganese nitrate) is highly crystalline and not a good active material in Li primary batteries. It exhibits a very low capacity ($\approx 1/3$) compared to γ-MnO_2 heat-treated in the range from 350 to 400 °C [1–9]. This difference is attributed to the smaller particle size and strain in the particles of β-MnO_2 synthesized by heat treatment of γ-MnO_2 (whether produced electrically, chemically, or by acid digestion) [17].

2.5   Discharge Mechanism

The open-circuit voltage of Li/MnO_2 is about 3.5 V [1,4,27], and its theoretical capacity is 308 mAh/g [1]. Thus, its theoretical energy density is about 1080 Wh/kg. The typical working voltage is about 3.0 V, with a cutoff voltage of 2 V (most of the cell capacity has been expended at 2 V). Capacities range from 160 to 230 mAh/g at low current rates after heat treatment (350 to 400 °C) for both EMD and CMD [1,3–8,27].

Based on x-ray diffraction, atomic absorption spectroscopy, and ion microanalysis, Ikeda et al [3,4] determined that the overall reaction between Li and the heat-treated MnO_2 is an intercalation reaction:

$$Li + Mn^{+4}O_2 \rightarrow Li^+Mn^{+3}O_2. \tag{1}$$
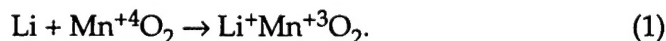
The $Li^+Mn^{+3}O_2$ indicates that the Li ion is intercalated in the MnO_2 lattice and results in Mn being reduced from +4 to +3 [3,4]. This mechanism has been confirmed by other investigators [6,7].

The amount of Li intercalated (eq (1)) is a function of the Mn^{+4} concentration. Thus, for high-capacity MnO_2, it is preferred that all the Mn be in the +4 state. In CMD and EMD, nearly all the Mn is in the +4 state; hence, high capacity is achieved [2,4].

As stated earlier, the concentration of Mn^{+4} ions is reduced when structural water is present, and thus a decrease in capacity is exhibited. Since CMD contains less structural water than EMD, its capacity (all other things being equal) should be higher than that of EMD. The capacity difference between CMD and EMD based on the structural water difference is estimated to be about 5 percent.

The discharge capacity of heat-treated γ-MnO_2 formed by acid digestion of $LiMn_2O_4$ is comparable to or slightly exceeds the capacity of heat-treated EMD [17]. This difference may be attributed to the lower structural water content of the acid-digested material compared to EMD after

high-temperature heat treatment (see sect. 2.4). When Li is discharged into MnO_2, it resides in the $[1\times1]$ and/or $[1\times2]$ channels in the MnO_2 structure, with most of it in the $[1\times2]$ channels.

2.6 Catalytic Behavior

MnO_2 is widely used by itself as a catalyst for selective oxidation of many organic compounds in neutral media [28–30], including alcohols, amines, hydrazines, and hydrocarbons. Most of these reactions proceed at reasonable rates at room temperature. The oxidation mechanism consists of (i) adsorption of the reactants onto the MnO_2 surface, (ii) oxidation, and (iii) desorption of the product.

The oxidizing power of MnO_2 has been shown [28,29,31] to be a function of particle size, purity, and water content. In general, as the particle size and purity decrease, an increase in the reaction rate is observed. For the third factor, water content, it is structural water present as OH^- groups that controls the catalytic behavior of MnO_2. Kanungo [31] has shown a direct relationship between the amount of structural water and the catalytic behavior of MnO_2. The catalytic behavior (rate of reaction) increased initially with an increase in the amount of OH^-. However, at large OH^- concentrations, the activity of the catalyst increased very little with increasing OH^- [31]. Kanungo suggested that OH^- groups must be present for MnO_2 to act as a catalyst; therefore, completely dehydroxylated MnO_2 is not an active catalyst for oxidation. The catalytic behavior of MnO_2 is related to electron transfer from an Mn^{+3} ion associated with an OH^- group to an Mn^{+4} ion [31]. Kanungo's results revealed that physically absorbed water (neutral molecules) did not influence the catalytic behavior of MnO_2.

3. Swelling (Gassing) Problem

A review of the literature reveals that swelling (gassing) in Li/MnO_2 cells during storage before discharging has been reported for an electrolyte alone [32] and for an electrolyte with an Li anode and MnO_2 cathode [14,33–38]. In addition, swelling has been observed during deep discharge in an Li/MnO_2 cell [39–41]. The cell components, observed gases, and possible reaction mechanism(s) for gas generation are listed in table 1. All these observations were reported after the U.S. patent of Ikeda et al in 1979 [2], who developed the heat treatment for MnO_2 that allowed it to be used in nonaqueous cells. The heat treatment was intended to remove all the physically absorbed and most of the structural water and obtain a proper structure for MnO_2, so that it could act as a stable active cathode in a cell with an Li anode and lithium salt dissolved in an organic solvent, and exhibit no gas evolution during storage.

Table 1. Gas generation.

Ref	Components[a]	Gases generated[b]	Potential reaction mechanism(s)
32	$LiClO_4$:PC	None	—
32	$LiClO_4$:PC + $HClO_4$ (trace)	CO_2	PC hydrolysis
33	Li/$LiClO_4$:PC-DME/MnO_2	CO_2 (significant) H_2 (insignificant)	PC hydrolysis Li reaction with water
14	Li/$LiN(SO_2CF_3)_2$:PC-DME-DOL/MnO_2	CO_2 (significant) H_2 (significant)	PC hydrolysis Li reaction with water
37	Li/Dry[c] PC or DME or DOL or THF/MnO_2	None	—
37	Li/Wet PC or DME or DOL or THF/MnO_2 Li/Wet DOL/MnO_2	H_2 (significant) CO_2 (significant)	Li reaction with water DOL hydrolysis
38	Li/PC/MnO_2	CO_2 (significant)	MnO_2 catalysis
39	Li/$LiClO_4$:PC-DME/MnO_2	CH_4[d]	Oxidation

[a]*PC = propylene carbonate, DME = dimethoxyethane, DOL = dioxolane, THF = tetrahydrofuran.*
[b]*Significant concentrations are flagged.*
[c]*Dry = <25 ppm water.*
[d]*Only during discharge.*

3.1 Gas Evolution from an Electrolyte Alone

Hlavaty and Novak [32] investigated the reaction of $LiClO_4$ with propylene carbonate (PC). They observed that after one year almost no reaction occurred between $LiClO_4$ and PC. No gases were detected. However, if a small amount of $HClO_4$ was added to the $LiClO_4$/PC solution, PC decomposed relatively quickly into CO_2 and 1,2 propandiol. They suggested that the presence of protons increased the decomposition rate of PC. They also observed that the addition of excess pyrrole inhibited decomposition of PC even in the presence of $HClO_4$. They attributed this effect to the protonation of the pyrrole nitrogen, which removed the protons from the solution.

Relevance to pouch cell swelling. It is possible for a lithium salt to react with water physically absorbed on the surface of the MnO_2 cathode (this includes the binder and conductive agent) or present in the solvents to form an acid. The acid can then act as a catalyst for hydrolysis of PC, resulting in the formation of CO_2 and 1,2 propandiol. Thus, if PC is used as a solvent and water is available in the system, it is possible, depending on the lithium salt present, for CO_2 gas to be formed during storage without any electrodes present.

3.2 Gas Evolution during Storage of an Li/MnO_2 Cell (Duracell)

Moses et al [33] observed swelling in a sealed cell of Li/1 M $LiClO_4$ in 1:1 PC-dimethoxyethane (DME)/MnO_2 (90% β, 10% γ), graphite, and teflon, during accelerated testing at elevated temperature when the cathode

6

mixture (MnO_2 (90-percent β, 10-percent γ), graphite, teflon) was heated to less than 300 °C. Accelerated testing consisted of heating a sealed cell at 115 °C for 1 hour, followed by cooling to room temperature. If the cathode mixture was heated at temperatures close to 300 °C, the expansion of the cell was about 5 percent, compared to 30 percent at 200 °C. The water content of the electrolyte was kept below 50 ppm.

Moses et al [33] evaluated the behavior of each component in the cell by assembling a series of dummy cells with various components left out and then evaluating the gassing characteristics. Their results revealed that the expansion of the cell was mainly due to the MnO_2 cathode, PC, and (to a lesser extent) $LiClO_4$. They observed that elimination of the Li anode had very little effect on the amount of gas generated during storage.

Gas analysis of Li/MnO_2 cells revealed the presence of H_2 and CO_2. No quantitative results were given. However, an analysis of the area under the peaks (fig. 4 of Moses et al [33]) reveals that the area under the CO_2 peak is about 8 to 9 times larger than for the H_2 peak. Moses et al observed that the amount of H_2 is the same for cells containing heat-treated and non-heat-treated MnO_2. They suggested that the H_2 came from a reaction of Li with trace moisture and did not contribute significantly to gassing of the stored cells. Moses et al attributed the detrimental swelling to CO_2 coming from the decomposition of PC. Further analysis revealed 1,2 propandiol and propylaldehyde as additional reaction products. The reaction products of CO_2 and 1,2 propandiol observed by Moses et al [33] are in agreement with those reported by Hlavaty and Novak [32].

Moses et al suggested that decomposition of PC (yielding CO_2 and 1,2 propandiol) occurred by surface-catalyzed hydrolysis. The adsorption reaction occurs most likely at or near sites where the concentration of reactive hydroxide groups in MnO_2 is highest. This suggestion is in agreement with the results of Kanungo [31], who observed that the catalytic behavior of MnO_2 was a function of the amount of structural water (see sect. 2.6).

Relevance to pouch cell swelling. These results are of extreme importance to the swelling of the Li/MnO_2 pouch cells, since PC is one of the suggested solvents. The results of Moses et al suggest that CO_2 is the major contributor to swelling during storage. CO_2 is formed as a consequence of PC hydrolysis. Hydrolysis is catalyzed by MnO_2 containing structural water (OH^-).

3.3 Gas Evolution during Storage of an Li/MnO_2 Cell

Christopher et al [14] investigated the gas evolution of (i) the electrolyte 0.75 M lithium imide in dioxolane (DOL)/DME/PC (50:40:10) alone, (ii) various combinations of the solvents with the Li and MnO_2 electrodes, and (iii) actual pouch cells, all after storage at room temperature for

various times. In addition, they investigated gas evolution of actual pouch cells that were discharged to different depths before storage.

They observed that if the solvents were exposed to air (under dry room conditions), they decomposed to some extent. The reaction of MnO_2 and PC produced a significant amount of CO_2 (in agreement with results of Moses et al [33]). The reaction of Li with each solvent, as well as in the electrolyte with the desired solvent combination (50:40:10), produced a significant amount of H_2. As shown by analysis of actual pouch cells, CO_2 and H_2 were the gases primarily responsible for the swelling. In pouch cells that were discharged to remove about 3 percent of the total capacity, no swelling occurred during storage (≈ 3 weeks). Gas analysis of the discharged cells revealed almost no CO_2 and a decrease in the amount of H_2 (no quantitative results were given).

Relevance to pouch cell swelling. These results confirm the importance of the reaction between PC and the MnO_2 cathode and suggest a method of reducing gas evolution (predischarge) (see sect. 5.3 for more details).

3.4   Gas Evolution during Storage of an Li/MnO_2 Cell

Atwater et al [37] investigated solvent degradation and gas evolution in Li/MnO_2 cells. The solvents were either pure or mixed together. The solvents investigated include (i) tetrahydrofuran (THF), (ii) PC, (iii) DME, and (iv) DOL. They were used in a dry condition (less than 25 ppm water) or with 0.1 percent water added (wet condition). Cells were tested containing solvents with and without anodes or cathodes.

The results revealed that when only solvent was present or was in the dry condition, no significant gas was generated. When the cell contained a lithium anode and was in the wet condition, hydrogen gas was detected. Wet chemical analysis showed the presence of hydroxide in the cells where H_2 was generated. CO_2 was observed only when the MnO_2 cathode was present in wet DOL. The results also revealed that as the amount of water in the cathode increased, the relative amount of CO_2 to H_2 increased. In addition, CO_2 and H_2 were found in cells containing both an anode and cathode and dry solvents, which were stored at room temperature for one year or at elevated temperature. These results suggest that Li/MnO_2 can cause decomposition of the electrolyte without the presence of water and that the decomposition is related to the catalytic behavior of MnO_2.

Relevance to pouch cell swelling. These results are of great relevance to the swelling of the Li/MnO_2 pouch cells, since PC, DME, THF, and DOL are the suggested solvents. They underscore the importance of having water-free solvents to minimize gas evolution. The results reveal that CO_2 is generated only with water, DOL, and MnO_2 present. In addition, the

results suggest that even if water-free solvents are used, it is possible for the cells to swell in storage as a result of the catalytic behavior of MnO_2.

3.5 Gas Evolution during Storage of an Li/MnO$_2$ Pouch Cell (BlueStar)

Almond et al [38] observed that when Li/MnO_2 pouch cells were stored at elevated temperature, both electrolyte leakage and CO_2 generation occurred. They suggest that the CO_2 was caused by a reaction of the MnO_2 cathode with PC. They found that the amount of gas generation was dependent on the amount of predischarge. After a 7-percent predischarge, there was a dramatic reduction of the CO_2 concentration. Almond et al suggest that predischarging reduces the oxidation state of manganese, which in turn reduces the amount of PC that is decomposed.

Relevance to pouch cell swelling. These results further confirm the importance of the reaction between PC and the MnO_2 cathode and the use of predischarging as a means to reduce gas evolution.

3.6 Gas Evolution during Discharge of an Li/MnO$_2$ Cell

Skarstad and Merritt [39] observed swelling during discharging of sealed cells of $Li/1$ M $LiClO_4$ in 1:1 PC-DME/MnO_2. They observed that cells swelled (formed gas) only after 2 Ah of the 2.7-Ah cell capacity was withdrawn (that is, a 75-percent discharge). Examination of the discharged cells revealed the following solid products near the Li anode: Li_2C_2, LiH, LiOH, and Li_2CO_3.

To investigate gas formation during discharge, Skarstad and Merritt used a mixture of deuterated DME and unlabeled PC. Gas analysis revealed methane (CD_3H) as the sole gaseous product. Skarstad and Merritt suggested that the carbon atom and the three deuterium atoms came from a terminal methyl group of DME. They assert [39] that the other hydrogen atom must come from a source other than DME, but do not identify this source. They also suggest that the amount of gas is a function of the quantity of water, the quantity of MnO_2, and the concentration of DME (without, unfortunately, giving details). In a later patent, Merritt [40] suggested that decomposition of DME into methane during discharging was aided by the presence of absorbed moisture in the cell; he showed a significant decrease in the amount of methane gas as the absorbed water content decreased. It is notable that Skarstad and Merritt reported no swelling before discharging.

Crespi [41] has also observed gas generation during discharge of $Li/1$ M $LiClO_4$ in 1:1 PC-DME/MnO_2 cells. She suggests that the gas was methane coming from the breakdown of the electrolyte solvents as the cell was discharged. The specific solvent(s) was not specified. Crespi implies that

moisture in the cells aided the breakdown of the solvents. (Crespi [41] and Skarstad and Merritt [39,40] are from the same company.)

Relevance to pouch cell swelling. The results of Skarstad and Merritt are relevant to the swelling of the Li/MnO_2 pouch cells, since DME is one of the suggested solvents. In addition, their results plus those of Crespi reveal the importance of absorbed water on gassing. However, neither Skarstad and Merritt [39,40] nor Crespi [41] report any swelling (gassing) problems during storage. They observed gassing only after a deep discharge.

3.7 Decomposition of Dioxolane

It has been shown that a 2.5 M $LiClO_4$/DOL solution exhibited polymerization at 3.25 V versus Li/Li^+ [42]. The open-circuit voltage (OCV) of Li/MnO_2 is about 3.5 V. In addition, polymerization of DOL has been induced at room temperature by Lewis acids and even neutral alumina [43]. In this case, the decomposition species were polyethers, and the presence of water in DOL accelerated its decomposition [43]. However, nothing was reported about gas evolution as a result of DOL polymerization.

4. Summary of Literature on Gas Evolution

A review of the existing literature suggests that gas evolution of the Li/MnO_2 cells is due to the breakdown of the solvents.

1. PC undergoes a hydrolysis reaction to form CO_2. This reaction is a function of (i) the amount of absorbed water on the MnO_2 cathode (including binder/conductive agent) and in the solvents and (ii) the structural water. The catalytic activity of MnO_2 is dependent on the amount of structural water. The hydrolysis reaction can occur during storage.

2. For DME, the formation of CH_4 is most likely an oxidation reaction mediated by free radicals produced by electrochemical oxidation of the salts/solvents. The experimental data suggest that the reaction is a function of the absorbed water content and occurs only during discharging.

3. Gas generation is a strong function of (i) the absorbed water content of the solvents and cathode (including binder/electronic conductor), (ii) the structural water content of MnO_2, (iii) the type of salt, and (iv) the type of solvent.

More experimental work is required to confirm the above suggestions.

5. Potential Solutions to Swelling Problem

Several approaches have been suggested to solving the problem of gas generation during storage in the Li/MnO_2 system. These suggestions have primarily focused on modifying the electrolyte (the salt and solvent) and the MnO_2 cathode.

5.1   Salt

Moses [35] used accelerated testing at high temperature to show that the use of $LiPF_6$ instead of $LiClO_4$ resulted in a decrease in cell expansion from 33 to 5 percent for the same solvent (PC/DME) and a heat-treated MnO_2 cathode. A disadvantage of using Li salts with inorganic perhalogenated anions (such as $LiPF_6$) is that the anions can disproportionate into LiF and the conjugate Lewis acid in the solvent, as shown below for $LiPF_6$ [44]:

$$Li^+ + PF_6^- \rightarrow PF_5 + LiF . \qquad (2)$$
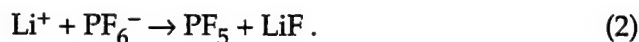
PF_5 can then react with water:

$$PF_5 + H_2O \rightarrow 2HF + POF_3 . \qquad (3)$$
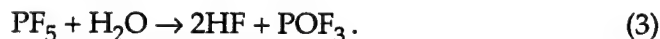
The HF acid can be a catalyst for PC hydrolysis, resulting in the generation of CO_2 and 1,2 propandiol.

5.2   Solvent

A review of the literature suggests that of the solvents used in the Li/MnO_2 pouch cells—PC, DME, DOL, and THF [13,14]—the one most responsible for gassing on storage is PC. To definitively confirm the suggestion that PC is the major contributor requires more experimental data.

It is possible that decomposition of the other solvents also contributes to gas evolution on storage. From the literature it is apparent that whatever the solvent, one of the variables influencing its decomposition is its absorbed water content. Thus, an obvious way to minimize decomposition of the solvents during storage is to use solvents that have the lowest possible water content. It has been suggested that a water scavenger be added to the electrolyte, such as a hydrophilic zeolite or a hydrophilic cellulosic material [45].

11

5.3 Cathode

To minimize gassing during storage, it is important that the MnO_2 cathode's water content, both absorbed and structural, be reduced as low as possible. A simple way is to use the heat treatment described in the U.S. patent of Ikeda et al [2]. Ideka reports [4] that after the heat treatment specified in the patent, the cell did not gas after two years of storage at room temperature (electrolyte: $LiClO_4$ in PC/DME). Ikeda states that some structural water is present in MnO_2 after the heat treatment (about 1 to 2 wt.%), but that this has no effect on the storage characteristics [4]. However, the cell used by Ikeda was contained in a stainless steel can, not in the more susceptible pouch cell. Therefore, even if the MnO_2 were given the patented heat treatment [2], it is highly possible that this would not be sufficient to prevent gassing of pouch cells during storage, because the MnO_2 would still contain 1 to 2 wt.% structural water.

There are several different ways to reduce the structural and absorbed water content associated with the MnO_2 cathode:

1. Instead of EMD and CMD, use γ-MnO_2 formed by acid digestion of $LiMn_2O_4$, since it has a lower structural water content (0.1 versus 1 wt.%) and a similar discharge capacity [17].

2. Moses [34] suggests adding lithium nitrate or calcium nitrate to MnO_2. Moses suggests that these additives reduce the reactivity of surface functional groups (OH^-) on the cathode surface for decomposition of the solvents. However, he gives no details on how this occurs. Moses' results revealed that the addition of 0.1 wt.% of lithium nitrate to MnO_2 (not heated to 300 °C) reduced the swelling to almost zero, with the same capacity as MnO_2 that was heated to 300 °C. At higher additive concentrations, however, a reduction in capacity may result.

3. It may be possible to reduce the absorbed water content associated with the MnO_2 cathode by the addition of an insoluble desiccant to the MnO_2 cathode mixture. Merritt [39] has shown that the addition of P_2O_5 significantly reduced (by 90 percent) the amount of methane gas generated during discharge. The amount of P_2O_5 was not given, but it is likely to be in the range from 0.5 to 2 wt.% [40]. Merritt suggested that as the cell discharged, lithium ions moved into the lattice MnO_2 and caused absorbed water to be released. The desiccant tied up the liberated water and thus prevented it from reacting with the solvent to form gas.

4. Another way to reduce the absorbed water content of the MnO_2 cathode and retard gas formation during discharge is to mix a minor amount (15 to 35 wt.%) of V_6O_{13} into the cathode material (MnO_2, conductive agent, and binder). The addition of V_6O_{13} not only reduces gas formation during discharge but also provides an additional reactive cathode material.

Crespi [41] showed that the addition of 22 wt.% V_6O_{13} reduced gas formation (methane) to almost zero during discharging of Li/MnO_2 cells. No mention was made of the change in cell capacity as a result of the addition of V_6O_{13}, nor of how its addition reduced gas formation.

5. A method of reducing the water content of the MnO_2 cathode, particularly structural water, is reactive dehydration [46]. For example, Marincic and Fuksa [46] suggest placing MnO_2 in a fluid desiccant such as thionyl chloride alone or thionyl chloride containing a small amount of a dissolved solute, such as aluminum chloride. The thionyl chloride reacts with water to form SO_2 and HCl, both of which are removed from MnO_2 under vacuum. X-ray diffraction of MnO_2 and infrared spectra of the electrolyte before and after the thionyl chloride treatment revealed that structural water had been removed. However, no quantitative results were given. In addition, no tests were conducted to determine if the reactive dehydration treatment improved electrochemical performance or affected storage behavior (gassing).

6. Another way to reduce gassing in a cell is predischarging the cell of up to 5 percent of its capacity before storage [36]. Taylor [36] has suggested that predischarging the cell reduces the amount of absorbed water associated with the MnO_2 cathode according to the following reaction:

$$2e^- + MnO_2 \text{ (active)} \cdot H_2O + 2 Li^+ \rightarrow Li_2O + H_2 + MnO_2 \text{ (inactive).} \qquad (4)$$
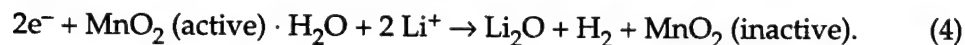
The reaction causes MnO_2 to change from an active to an inactive catalyst for solvent (e.g., PC) decomposition. Taylor states that as long as the absorbed water content is less than 1 wt.%, the amount of hydrogen gas evolved (eq (6)) is relatively minor compared to the amount of gas from decomposition of the solvents. However, if the absorbed water content is above 1 wt.%, significant loss of capacity and hydrogen gas evolution will occur during discharging. It is interesting that Taylor identified the catalytic activity of MnO_2 with absorbed water, whereas others associated it with structural water [28,30,31,33].

7. Another potential solution is to replace the MnO_2 cathode with another cathode (such as another oxide—e.g., lead oxide [36]) that may not act as a catalyst for decomposition of the solvents—particularly one that does not show enhanced catalytic behavior in the presence of water (structural and absorbed).

13

6. Li/MnO$_2$ Self-Discharge: Literature Review

A second phenomenon that occurs during storage of the Li/MnO$_2$ system is a loss of capacity resulting from self-discharge. A survey of the literature concerning self-discharge in the Li/MnO$_2$ system indicates three primary factors:

- the oxidation state of the manganese ion,

- the nature of the salt used in the electrolyte and the amount of absorbed water in the salt, and

- the nature of the solvent.

The discharge curves for Li/1 M LiClO$_4$ in PC/DME/MnO$_2$ (EMD) sealed cells as a function of storage time at room temperature revealed a self-discharge ratio of about 1 percent per year [4]. Ikeda's results [4] also revealed that after 6 months of storage at room temperature, the solubility of MnO$_2$ (Mn content) in the electrolyte was less than 1 ppm.

The self-discharge of Li/MnO$_2$ appears strongly related to manganese-ion dissolution as a result of acid attack [47–51]. The amount of dissolution is a function of (i) the oxidation state of the manganese ion, (ii) the nature of the salt and amount of absorbed water, and (iii) the nature of the solvent. Mao et al [48] have shown that as the oxidation state of the maganese ion increased, the dissolution rate (amount of Mn deposited on the lithium anode) decreased in Li/1 M LiPF$_6$ in EC/DEC/manganese oxide cells held at 4.2 V. For example, Li$_2$MnO$_4$ (Mn = +4) exhibited no dissolution at all, whereas MnO (Mn = +2) was highly dissolved. Based on these results, it would be expected in a first approximation that the dissolution rate (and hence self-discharge) would not be a significant problem in MnO$_2$, since almost all the Mn in MnO$_2$ is in the +4 state for both CMD and EMD. Of these two, CMD would probably have a lower self-discharge rate than EMD, as a result of its lower structural water content and hence higher Mn^{+4} content (see sect. 2.3 and 2.5).

The dissolution of the manganese ion in the +2 state has been shown to be a function of the nature of the salt and the amount of absorbed water [47–51]. Mao et al [48] have shown that the dissolution rates for various salts in EC/DEC in Li/Li$_x$Mn$_2$O$_4$ cells are ordered as follows:

$$LiClO_4 > LiPF_6 > LiN(SO_2CF_3)_2 > LiBF_4. \tag{5}$$

Jang and Oh [47] have shown that the dissolution rates (Mn^{+2} content in the electrolyte) for various salts in PC/DME in Li/Li$_x$Mn$_2$O$_4$ cells are ordered as

$$LiCF_3SO_3 > LiPF_6 > LiClO_4 > LiAsF_6 > LiBF_4. \tag{6}$$
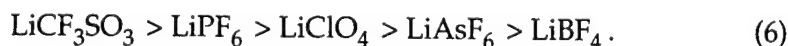
Nohoma et al [49] reported that after 40 days of storage at 60 °C (equivalent to 2 years at room temperature), the discharge capacity decreased $\approx$7 percent for $LiClO_4$, $LiAsF_6$, and $LiCF_3SO_3$, $\approx$18 percent for $LiPF_6$, and $\approx$44 percent for $LiBF_4$ in $Li/salt/PC/DME/MnO_2$ cells. Elemental analysis of the lithium electrode revealed significant Mn on the surface for $LiBF_4$. These results are in contrast to those of Mao et al [48] and Jang and Oh [47], who observed that $LiBF_4$ was the least corrosive salt. Furthermore, Jang and Oh and Nohoma et al suggest that $LiPF_6$ is more corrosive than $LiClO_4$. This is in contrast to the results of Mao et al [48]. Jang and Oh suggested that dissolution of the spinel (Mn^{+2} ions) is a result of protons generated during oxidation of the solvent. Jang and Oh postulate that $LiClO_4$ and $LiCF_3SO_3$ are more susceptible to electrochemical oxidation than the fluorinated salts; electrochemical oxidation results in the formation of free radicals, which cause solvent oxidation and hence protons. The analysis by Nohoma et al of the $LiPF_6$ solution after 40 days at 60 °C revealed the presence of diglyme, triglyme, and tetraglyme in addition to PC and DME. They suggested that the glymes formed as a result of the decomposition of DME by PF_5, which formed from the disproportionation of $LiPF_6$ into LiF and PF_5 (eq (2)).

Mao et al [48] showed that the dissolution behavior is a strong function of the absorbed water content for $LiPF_6$. Adding water to $LiPF_6$ increased the dissolution rate. This result is expected based on equation (2) and

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF ; \qquad (7)$$
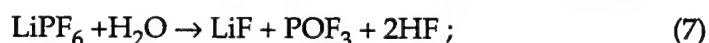
these two equations reveal that the addition of water increases the amount of HF; hence an increased dissolution rate should be exhibited. Mao et al observed that the dissolution rate decreased when ammonia was added, which neutralized the HF. Based on the above results, the preferred salt for the Li/MnO_2 pouch cells to minimize self-discharge of the three suggested salts ($LiCF_3SO_3$ or $LiClO_4$ or $LiN(SO_2CF_3)_2$) is $LiN(SO_2CF_3)_2$ (lithium imide) [13].

The self-discharge rate (sometimes related to the dissolution behavior) has been observed to be a function of the electrolyte solvent [47–52]. For example, Nohoma et al [49] observed for a given salt, $LiCF_3SO_3$, that the discharge capacity after 40 days at 60 °C showed the smallest decrease in an EC/DME solution ($\approx$4 percent), compared to 7 percent in PC/DME and $\approx$18 percent in PC/THF (the largest decrease). No explanations for this difference were given. Jang and Oh [47] also showed that the dissolution rate of $Li_xMn_2O_4$ was a function of solvent type. They observed that for $Li_xMn_2O_4$ at potentials between 3.6 and 4.2 V (vs Li/Li^+), the Mn^{+2} content in the electrolyte ($LiClO_4$ salt) was higher for ethers (THF and DME) than for carbonates (PC and DEC). Of the two ethers, THF exhibited a higher dissolution rate than DME. This result is in agreement with those of Nohoma et al [49]. It should be noted that these results were obtained above 3.6 V, whereas the voltage range of Li/MnO_2 is signifi-

cantly lower: 2.2 to 3.5 V. Nevertheless, it is interesting that the results of the dissolution studies suggest that DME is more susceptible to oxidation than PC. This agrees with the results of Skarstad and Merritt [39,40] and Crespi [41], which reveal that gas generation during discharge results from oxidation of DME. In addition, Frackowiak and Kuksenko [52] have shown that the addition of DME to PC decreased the storage capacity from 2 to 3 percent after 30 days at 45 °C. They suggested that polymerization of DME oxidation products on the MnO_2 surface blocks the electrolyte from entering the porous cathode, resulting in a voltage decrease.

In summary, the self-discharge of Li/MnO_2 is a function of (i) the oxidation state of the manganese ion, (ii) the nature of the salt and amount of absorbed water, and (iii) the nature of the solvent. Since almost all the manganese is in the +4 state for CMD and EMD, the self-discharge rate for both should be low. The self-discharge rate for CMD would be expected to be slightly less than for EMD. Self-discharge is higher for $LiClO_4$ and $LiCF_3SO_3$ electrolytes than for fluorinated salt electrolytes, because they form free radicals during electrochemical oxidation that mediate solvent oxidation; electrolytes containing fluorinated salts are relatively inert to electrochemical oxidation. However, self-discharge for fluorinated salts is a function of the water content. Self-discharge is higher for ethers (e.g., DME) than for carbonates (e.g., PC) because ethers are more susceptible to oxidation.

7. Conclusions

A review of the existing literature suggests that gas evolution of the Li/MnO_2 cells is due to the breakdown of the solvents.

1. PC undergoes a hydrolysis reaction to form CO_2. This reaction is a function of (i) the amount of absorbed water on the MnO_2 cathode (including binder/conductive agent) and in the solvents and (ii) the structural water. The catalytic activity of MnO_2 is dependent on the amount of structural water. The hydrolysis reaction can occur during storage.

2. For DME, the formation of CH_4 is mostly likely an oxidation reaction mediated via free radicals produced by electrochemical oxidation of the salts/solvents. The experimental data suggest that the reaction is a function of the absorbed water content and occurs only during discharging.

3. Gas generation is a strong function of (i) the absorbed water content of the solvents and cathode (including binder/electronic conductor), (ii) the structural water content of MnO_2, (iii) the type of salt, and (iv) the type of solvent.

4. Of the suggested solvents (PC, DME, DOL, THF) for use in Li/MnO_2 pouch cells, the literature suggests that the major contributor to gassing

during storage is PC. However, much more experimental evidence is necessary to definitely confirm this suggestion.

5. Less gassing on storage is expected for CMD than for EMD. However, this difference might not be significant. The difference is a result of the lower structural water content associated with CMD. Along these lines, one should try γ-MnO_2 that is formed by acid digestion of $LiMn_2O_4$ (instead of using EMD and CMD) since it has a lower structural water content (0.1 versus 1 wt.%) and a similar discharge capacity.

6. Predischarging, use of water scavengers, cathode additives, reactive dehydration, properly heat-treated MnO_2, weak oxidizing salts, and oxidation-resistant solvents may help eliminate gassing on storage.

7. Self-discharge of Li/MnO_2 is a function of (i) the oxidation state of the manganese ion, (ii) the nature of the salt and amount of absorbed water, and (iii) the nature of the solvent. Since almost all the manganese is in the +4 state for CMD and EMD, the self-discharge rate for both should be low. The self-discharge rate for CMD would probably be slightly less than for EMD. Self-discharge is higher for $LiClO_4$ and $LiCF_3SO_3$ electrolytes than for fluorinated salt electrolytes, because they form free radicals during electrochemical oxidation that mediate solvent oxidation; electrolytes containing fluorinated salts are relatively inert to electrochemical oxidation. However, self-discharge for fluorinated salts is a function of the water content. Self-discharge is higher for ethers (e.g., DME) than for carbonates (e.g., PC) because ethers are more susceptible to oxidation.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE December 1998	3. REPORT TYPE AND DATES COVERED Final, 10/97–9/98

4. TITLE AND SUBTITLE Gas Evolution and Self-Discharge in Li/MnO$_2$ Primary Batteries

6. AUTHOR(S) Jeffrey Wolfenstine, Donald Foster, Wishvender Behl, and Sol Gilman

5. FUNDING NUMBERS

DA PR: AH47

PE: 61102A

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
Attn: AMSRL-SE-DC   email: jef_wolfenstine@stinger.arl.mil
2800 Powder Mill Road
Adelphi, MD 20783-1197

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-1805

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
2800 Powder Mill Road
Adelphi, MD 20783-1197

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
ARL PR: 8NENYY
AMS code: 611102.H47

12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A survey is presented of the available literature on the problem of gas evolution in the Li/MnO$_2$ primary battery system during storage. This gassing is due to the breakdown of the solvents, primarily propylene carbonate (PC) and dimethoxyethane (DME). Of these, the major contributor to gassing during storage is PC, which undergoes a hydrolysis reaction to form CO$_2$. This reaction is a function of the amount of absorbed and structural water. Techniques to help eliminate gassing during storage include predischarging and the use of water scavengers, cathode additives, reactive dehydration, properly heat-treated MnO$_2$, weak oxidizing salts, and oxidation-resistant solvents.

Although not a major factor in gas evolution in stored batteries, DME has been observed to form methane (CH$_4$) during discharging, probably via an oxidation reaction that is ultimately a function of the absorbed water content. The report also briefly reviews the self-discharge characteristics of Li/MnO$_2$. Three factors determine the self-discharge of Li/MnO$_2$:
• The oxidation state of the manganese ion. For the types of MnO$_2$ used, it is expected that the self-discharge rate would be low.
• The nature of the electrolyte salt and amount of absorbed water. Self-discharge is higher for LiClO$_4$ and LiCF$_3$SO$_3$ electrolytes than for fluorinated salt electrolytes.
• The nature of the solvent. Self-discharge is higher for ethers (e.g., DME) than for carbonates (e.g., PC).

14. SUBJECT TERMS
Lithium, manganese dioxide

15. NUMBER OF PAGES
28

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT SAR

23